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► To cite this version:

Jean-Benoit Le Cam, Evelyne Toussaint. Cyclic volume changes in rubber. *Mechanics of Materials*, 2009, 41, pp.898-901. 10.1016/j.mechmat.2009.02.004 . hal-01131585

HAL Id: hal-01131585

<https://hal.science/hal-01131585>

Submitted on 16 Mar 2015

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Cyclic volume changes in rubber

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Abstract

The present paper deals with the volume variation in filled crystallizable natural (F-NR) and uncrystallizable styrene butadiene (F-SBR) rubbers subjected to cyclic loadings. During their deformation, such materials exhibit volume variation induced by the cavitation phenomenon and the decohesion between particles and the rubber matrix. In this study, we propose to measure this volume variation over the first mechanical cycles by an original full-field measurement technique. First, results show that in both filled compounds no residual change is observed. Moreover, after the first cycle, the response of both compounds is stabilized in terms of volume variation. However, a hysteresis loop is observed for the first cycle in F-SBR whereas it is observed for each cycle in F-NR. Finally, the measurement methods allow us to highlight the influence of stress-induced crystallization on the volume variation.

Key words: volume changes, natural rubber, styrene-butadiene rubber, cavitation

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1 Introduction

The deformation of rubbers induces a number of physical phenomena. Among them, polymer chain extensibility and failure, the ability of certain elastomers to crystallize under stress (Trabelsi *et al.*, 2003), decohesion between zinc oxides and the rubber matrix (Le Cam *et al.*, 2004) and cavitation in the rubber matrix or/and at the filler aggregate poles (Ball *et al.*, 1981; Diani, 2001; Gent and Lindley, 1958; Goebel and Tobolsky, 1971) seem to be the most significant. These phenomena are classically studied at the macroscopic scale in terms of volume variation. In the past, volume change $\frac{\Delta V}{V}$ was largely described in relation to the elongation λ (defined as the ratio between the current length and the initial length), see Mullins and Tobin (1957); Christensen and Hoeve (1970); Penn (1970); Shinomura and Takahashi (1970); Goebel and Tobolsky (1971). However, these studies do not allow to distinguish the influence of each phenomenon on volume variation. Moreover, in the studies above-mentioned, volume change is investigated over monotonic uniaxial tensile loading.

This study deals with the influence of uniaxial cyclic loading on volume variation. Indeed, cyclic loading generates significant variation of the mechanical properties, for instance the stress-softening described by Mullins (Mullins, 1948). Besides, in order to highlight the effect of stress-induced crystallization, two different carbon black filled compounds are considered here: a non-crystallizable styrene-butadiene rubber (F-SBR) and a crystallizable natural rubber (F-NR).

In the following, the materials and the sample geometry used are presented. Then, loading conditions and volume variation measurement are precisely de-

tailed. Finally, the evolution of volume variation during the first loading cycles is discussed by comparing crystallizable and uncrystallizable rubbers.

2 Experimental Section

2.1 *Materials and Sample*

In order to compare volume changes in F-SBR and F-NR, both compounds are filled with 34 parts per hundred of rubber in weight (phr) of carbon black. Table 1 summarizes their chemical composition and Table 2 some mechanical characteristics. F-NR and F-SBR are respectively cured for 7 min and 5 min, and the mold temperature is set at 160°C . To overcome aging problems, samples are frozen at -18°C 48 h after molding. They are then thawed out 24 h before testing. The samples are 30 mm long, 4 mm wide and 2 mm thick.

2.2 *Loading conditions*

Mechanical cycles are performed under prescribed uniaxial displacement with a 50N Instron 5543 testing machine. Hygrometry is equal to 34 % and the temperature of the room is set at 23°C . The corresponding stretch ratio varies between 1 and 3.1 for F-SBR samples and between 1 and 2.55 for F-NR samples. The strain rate is set at 1.3 min^{-1} for each test.

Table 1

Material Formulation (phr).

Components	NR	SBR
Rubber	100	100
Zinc oxide	9.85	10
Oil	3	0
Carbon black	34	34
Sulfur	3	3
Stearic acid	3	3
Antioxidant	2	5
Accelerators	4	4.3

Table 2

Mechanical properties.

Properties	NR	SBR
Density	1.13	1.12
Shore A hardness	58	67
Stress at break (MPa)	22.9	16.5
Elongation at break (%)	635	343

2.3 Volume variation measurement

The change in volume is deduced from the displacement fields on the sample surface obtained by the image correlation technique. It consists in correlating

the grey levels between two different images of a given zone. Each image corresponds to different stretch ratio levels. To improve the image contrast, suitable white paint is sprayed on the surface before testing samples. This leads to a black and white random gray field. This optical technique allows us to reach a resolution of 0.1 pixel corresponding to $5.9 \mu m$ and a spatial resolution (defined as the smallest distance between two independent points) of 10 pixels corresponding to $590 \mu m$. The software used for the correlation process is SeptD (Vacher *et al.*, 1999).

Figure 1 presents the overall view of the optical setup. It consists in a cooled 12-bit dynamic Sensicam camera connected to a personal computer in order to process image acquisition and data treatment with the SeptD software. A uniform light at the sample's surface is ensured by lamps. The charge-coupled device (CCD) of the camera has $1.4 \cdot 10^6$ joined pixels (1376×1040). The camera is fixed on a multidirectional adjustable support and the distance between the sample and the CCD matrix is about 60 cm . In this configuration, an area of $4 \times 81 \text{ mm}^2$ is within shot of the digital camera. The size of this zone is sufficient to calculate global displacement slopes in both horizontal and vertical directions.

The previous full-field measurements are now considered to calculate the volume variation of the samples at each step of loading. For each mechanical cycle test, 28 images are stored for both materials. The first image is taken as the reference and corresponds to the undeformed state. The other images correspond to successive deformed states. Because of the large deformations undergone by the material, the displacement fields for each deformed state cannot be calculated by correlating images from the reference image. Thus, the following method has been developed:

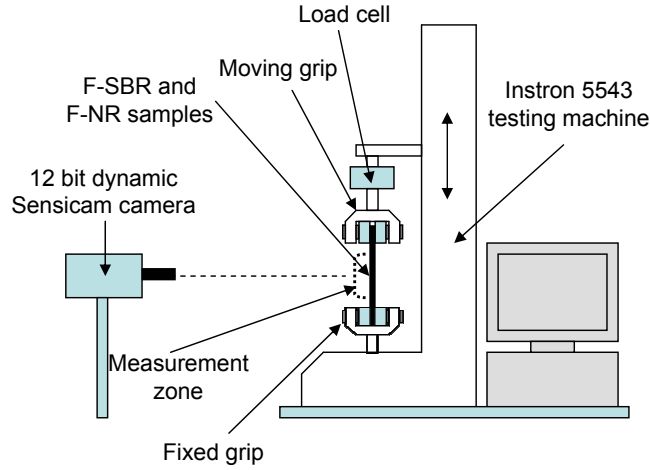


Fig. 1. Overall view of the optical setup

- (i) two successive images are correlated and the relative displacement fields are calculated with SeptD software. Between two images, a displacement of 3 mm is imposed by the moving grip. Then, relative displacement slopes in the horizontal and vertical directions are determined from Matlab software. In the present work, the material behavior is assumed to be transversely isotropic. This assumption has been checked from displacement calculated on the front and the side faces of the samples. So, relative stretch ratios and relative volume change can be calculated;
- (ii) finally, stretch ratios and volume variations are obtained by successive multiplications of the relative ones. This method has been validated by correlating the reference image and the last image of the cycle.

3 Results

In this section, the stress-stretch response and the corresponding volume variation measurements are first presented for F-SBR. Second, in order to compare

the two materials and more precisely to investigate the influence of stress-induced crystallization on volume variation, similar measurements are performed in F-NR.

3.1 Volume variation in F-SBR

Figure 2 presents the stress-stretch curves of F-SBR during the first three mechanical cycles. The material response exhibits the well-known stress softening described in the past by Mullins (Mullins, 1948): the stress and the area of the hysteresis loop decrease significantly between the first two cycles. Figure 3 presents the corresponding volume variation. This figure shows that relative volume changes in F-SBR do not exceed 1.10^{-1} for a 3.1 stretch ratio and that the maximum relative volume change is the same for the three cycles. The first cycle is the only one that exhibits a hysteresis loop, for volume change curve. No hysteresis loop is observed for the second and third cycles. Moreover, no significant residual volume variation is observed. Contrary to the nominal stress, the relative volume change can be considered as stabilized after the first cycle. To illustrate the latter, Figure 4 shows the volume change obtained during the third mechanical cycle. Here, no hysteresis loop is observed and the evolution of the volume variation versus the stretch ratio is linear. The last two results seem to indicate that phenomena involved in volume variation are different from those responsible for the stress softening.

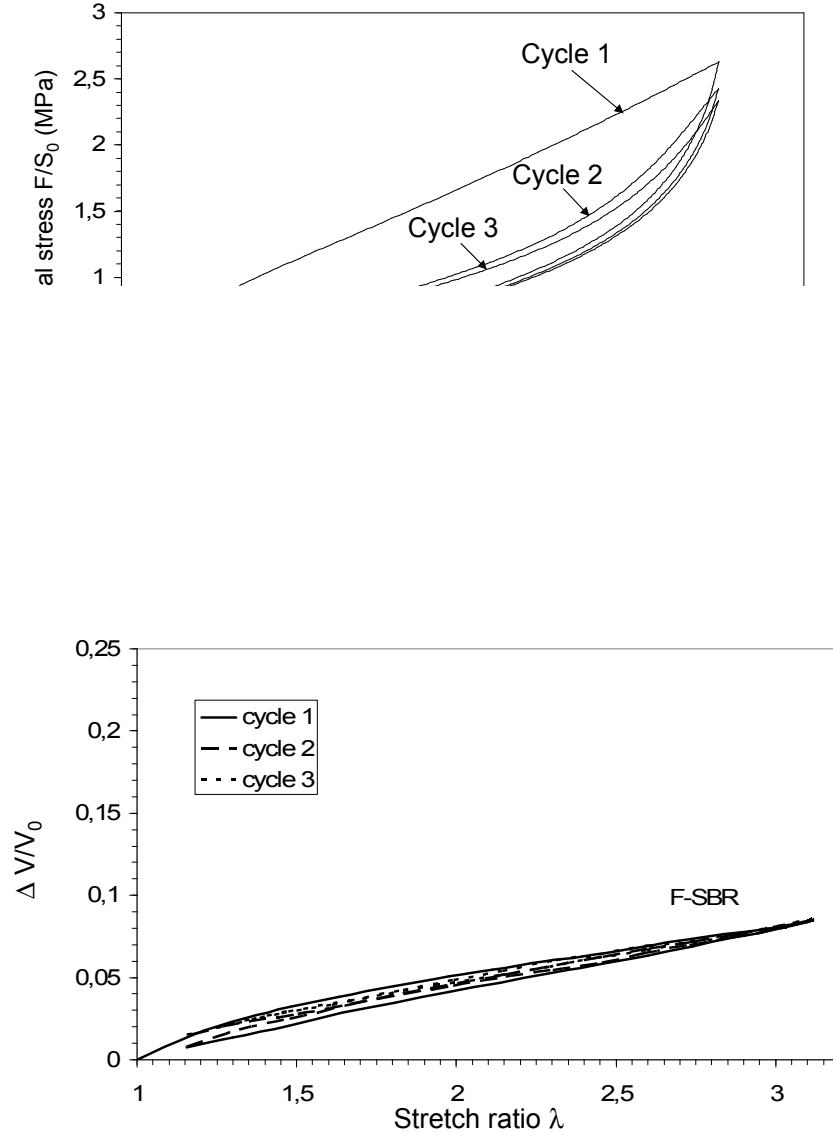


Fig. 3. The first mechanical cycle in F-SBR: volume variation

3.2 Volume variation in F-NR

In order to compare volume variation between F-SBR, i.e. uncrystallizable rubber and F-NR, i.e. crystallizable rubber, volume variation measurements are now performed in F-NR. Figure 5 presents the stress-stretch response of the material and Figure 6 shows the corresponding relative volume change. As expected, the stress-stretch curve exhibits the same stress-softening as in F-

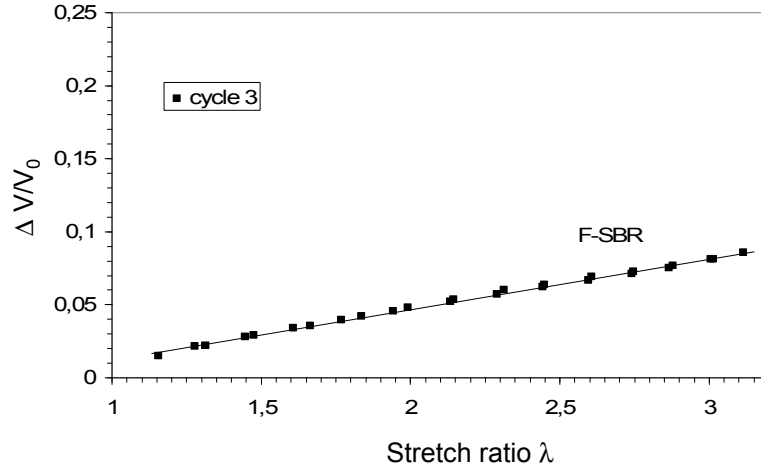


Fig. 4. Relative volume change during the third mechanical cycle in F-SBR

SBR. Similarly to F-SBR, stabilization of volume variation can be considered to occur after the first cycle. Here, the maximum volume variation reaches $2.4 \cdot 10^{-1}$ for a 2.55 stretch ratio. Contrarily to F-SBR, the hysteresis loop regarding volume change observed for the first cycle is also observed for the two following cycles, even if its size decreases between the two first cycles. This highlights the fact that the major part of the hysteresis loop in terms of volume variation is induced by crystallization. To investigate the latter result more precisely, Figures 7 and Figure 8 present the volume variation obtained during the first and the third cycles respectively.

Both figures highlight the fact that changes in the curve slope are observed for loading as well as for unloading. Moreover, these changes occur for the same stretch ratios. During the loading, the volume increases from the undeformed state due to formation and growth of cavities. From $\lambda = \lambda_{crystallization}$ on, the curve slope becomes lower. In fact, even if cavities grow continuously, crystallization starts and reduces the volume. This result is in good agreement with that of Trabelsi et al. (Trabelsi *et al.*, 2003). During the unloading, volume

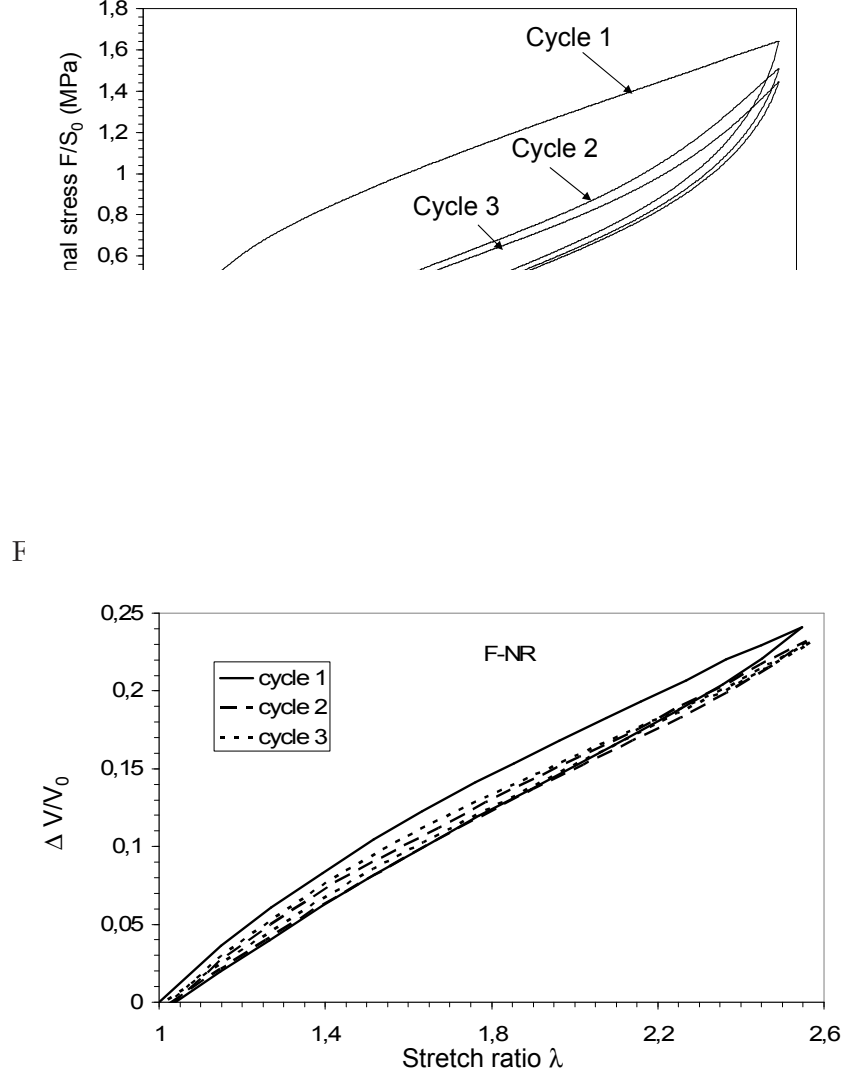
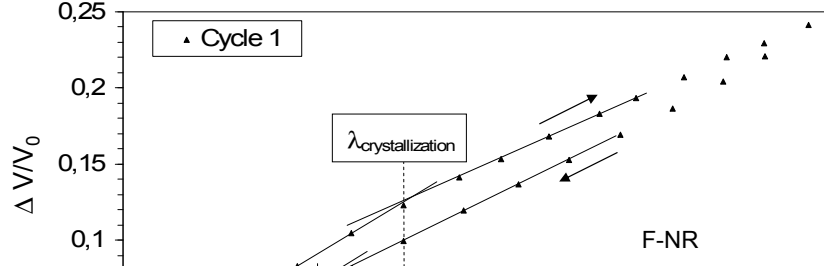


Fig. 6. The first mechanical cycle in F-NR: volume variation decreases with the cavity size, and melting of crystallites starts. The fact that for a given stretch ratio the volume is superior during loading than during unloading is mainly explained by the difference in the kinetics of crystallization and melting. During unloading, from $\lambda = \lambda_{melting}$, the melting of crystallites is complete, and volume decrease is only due to cavities closing. This explains why the curve slope increases.

The fact that the same characteristic stretch ratios are observed for the first and third cycles, i.e. $\lambda_{crystallization} = 1.6$ and $\lambda_{melting} = 1.4$, proves that Mullins



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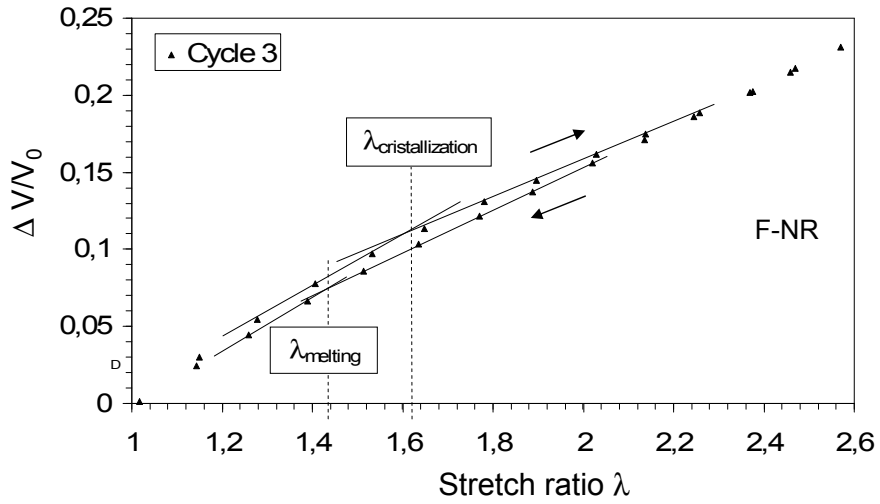


Fig. 8. Relative volume change during the third mechanical cycle in F-NR

effect does not influence the crystallization phenomenon. Moreover, the fact that no hysteresis loop is observed in terms of volume variation for the second and third cycles for non-crystallizable F-SBR seems to indicate that the hysteresis loop observed after the first cycle for crystallizable F-NR is only due to stress-induced crystallization.

4 Conclusion

This study investigates volume variation in rubbers under cyclic loading. Results show that volume variation under uniaxial tensile loading is a reversible process during the first three cycles. The fact that no residual change in volume is observed indicates that the mechanisms involved during volume variation are not the same as those contributing to stress-softening, i.e. the Mullins effect (Mullins, 1948). This is also highlighted by the fact that, contrary to the stress, the volume variation is stabilized after the first cycle. Moreover, in the case of filled natural rubber, stress-induced crystallization explains why a hysteresis loop is also observed in the volume variation curve for the second and the third cycles. More precisely, this loop results from the difference between crystallization and crystallite melting kinetics. Finally, the results obtained here lead to two issues of importance which remain unanswered. The first one is given by the fact that the present experiment has to be extended to a higher number of cycles, i.e. in the range of the fatigue domain. Thus, volume variation measurement could provide significant information on the frontier between reversible (quasi-static mechanisms) and irreversible (fatigue mechanisms) volume variation. The second one is the volume variation induced by multiaxial cyclic loadings. Further work in this field is currently being envisaged by the authors of this paper.

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